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EPR Studies on a Binitroxide Fullerene Derivative in the Ground Triplet and First Photoexcited Quintet State

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A fulleropyrrolidine with two covalently linked nitroxides has been studied by cw-EPR in its ground state and by TR-EPR and spin−echo detected EPR in the photoexcited state after pulsed laser excitation. The electron exchange interaction between the two unpaired electrons in the ground state is obtained from the analysis of the EPR spectra in the dark. The EPR signal of photoexcited samples consists of the superposition of the $Q_{(\pm 2)} \Leftrightarrow Q_{(\pm 1)}$ and of the $Q_{(\pm 1)} \Leftrightarrow Q_{(0)}$ transitions of the excited quintet state and of the signal due to the triplet state of the ground state biradical. The assignment to the quintet excited state was made by measuring the frequency of the echo detected transient nutation. Fourier transformation of the transient spectra along the microwave pulse length allowed us to disentangle the quintet transitions and to obtain precise measurements of the zero-field splitting parameters. The observed polarizations in the transient spectra are examined on the basis of selective intersystem crossing due to spin−orbit interaction and quintet−singlet mixing caused by the electron dipolar interaction.

Introduction

Transient paramagnetic species produced by shining short light pulses on molecules are usually generated with spin sublevels having population differences that can be orders of magnitude larger than that at thermal equilibrium. The system is said to be spin polarized, and the phenomenon is named chemically induced dynamic electron polarization (CIDEP). The Boltzmann equilibrium is reached in times of the order of microseconds by a spin−lattice relaxation process.

Time-resolved electron paramagnetic resonance (TR-EPR) spectroscopy exploits the strong spin polarization by recording the EPR signals of transient species in a short time interval after the light pulse. TR-EPR of transient free radicals and excited triplet molecules provided a deal of information on structure, dynamics, and chemical reactivity of these species, which are important intermediates in photochemical processes.[1−3]

TR-EPR observations of excited species with higher spin multiplicity are rare, even if quartet and quintet states were postulated a long time ago as transient intermediates in several photophysical processes, such as excited triplet quenching by free radicals and triplet−triplet annihilation.[4] The decacyclene anion radical is the only doublet state system exhibiting phosphorescence due to a metastable quartet state, which was observed by TR-EPR.[5]

A few years ago we investigated a class of C_{60} derivatives consisting of a fulleropyrrolidine (FP) adduct covalently linked to a stable nitroxide radical (TEMPO). In particular, we made the first observation of radical−triplet pairs in the quartet state in liquid solution[6] and in a glassy matrix.[7]

Both the photoexcited quartet and ground state of these adducts, after photoexcitation by a laser pulse, exhibit a strong spin polarization that derives from the M_S selective mixing between the Zeeman sublevels of Qr* and D* (quartet and doublet excited states). The mixing is due to the dipolar interaction between the unpaired electrons and is spin selective because the energies of Qr* and D* are separated by the exchange interaction J. The latter can be positive or negative and its sign determines the relative position of Qr* and D*. The sign of J could be inferred from the time evolution of the spin-polarized EPR lines (A→E for $J > 0$, E→A for $J < 0$).[8] For two similar derivatives, **1** and **2**, which differ only for the junction FP-TEMPO (Scheme 1), we observed that the exchange interaction has a different sign: positive for **1** and negative for **2**. The magnitude of J could not be determined from the TR-EPR results. However, in both cases it should be much larger than the nitrogen hyperfine coupling constant a_N because in liquid solution the TR-EPR spectrum of Qr* shows three lines whose separation is reduced to 1/3 that of the ground doublet state. Transient nutation experiments showed that in **1** the lower limit for J is the zero-field splitting parameter, ($|J| > |D|$).[9]

A bisadduct of C_{60} with two TEMPO substituted pyrrolidine rings at trans-3 positions has been investigated recently in the photoexcited state by a 2D nutation technique. While the ground state showed a doublet nature, because of a weak exchange interaction between the nitroxide unpaired electrons, a quintet excited state was observed.[10] In this paper we report the results of a study of a novel fulleropyrrolidine monoadduct, bearing two TEMPO units (Scheme 1, compound **3**), which has been

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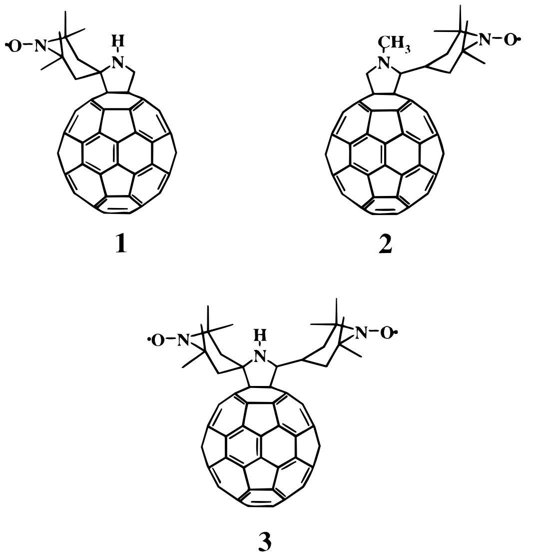
SCHEME 1



prepared and characterized. Derivative **3** combines the structural features of pyrrolidine **1** and **2** in one molecule. In fact, the pyrrolidine ring bears either spiro-linked (henceforth called n1) or nonspiro-linked (n2) TEMPO units at positions 5 and 2 of the ring, respectively. Derivative **3** could be prepared from C_{60}, glycine, 4-amino-4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TOAC),[11] and 4-formyl-4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-formyl-TEMPO)[12] in 30% yield via 1,3-dipolar cycloaddition of azomethine ylides to C_{60}.[13] Details of the synthesis and electrochemistry of derivative **3** will be reported elsewhere.[14]

Unlike the previous case,[10] in **3** the electronic ground state is split into a singlet S_G and a triplet T_G by the electron exchange interaction between the nitroxide unpaired electrons, while excited states with total spin S_T equal to 0, 1, and 2 (S, T, Q) are expected if the fullerene moiety is photoexcited in the triplet state. Moreover, the opposite sign of the exchange interaction between nitroxides and triplet fullerene is expected to reduce the energy separation between quintet Q and singlet S allowing for a possible strong mixing between them and consequently producing a large spin polarization.

In this paper we present the results of TR-EPR experiments on **3**, with evidence for both the observation of the Q state and the spin polarization of the triplet electronic ground state T_G. Transient nutation experiments were used for determining the spin multiplicity of the paramagnetic species responsible for the observed spin polarized spectra.

Experimental Section

Toluene solutions (ca. 10^{-4} M) of compound **3** were degassed by repeated pump−freeze−thaw cycles and sealed under vacuum in 4 mm o.d. quartz tubes. Steady-state and time-resolved EPR spectra were recorded with a Bruker ER 200 D X-band spectrometer equipped with a LeCroy 9450A digital oscilloscope used to collect and average the transient signals. A visible beam (582 nm) of a dye laser pumped by an excimer laser was used for the excitation. Details of the equipment and method were reported previously.[15]

Two-dimensional (2D) nutation and electron spin−echo (ESE) measurements were carried out on a homemade pulsed spectrometer. The second harmonic (532 nm) of an Nd:YAG laser was used for photoexcitation. Details of both the EPR technique and of the instrumentation are reported in the literature.[9]

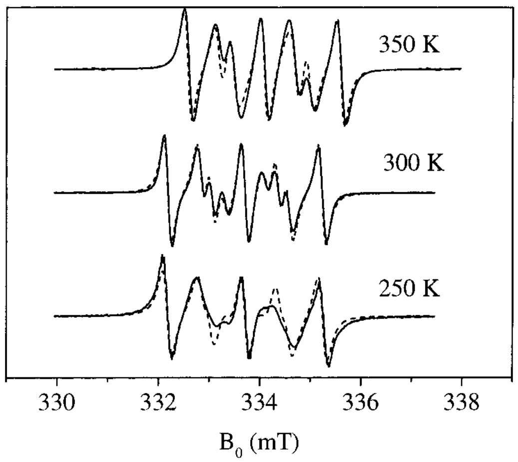


Figure 1. cw-EPR spectra of **3** in toluene at different temperatures. Solid line: experimental; dotted line: computer simulation.

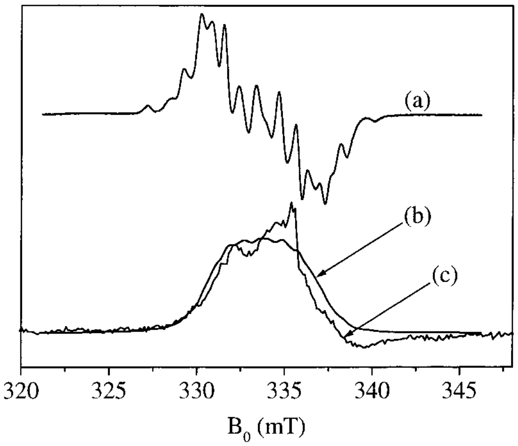


Figure 2. EPR spectra of **3** in toluene solution. (a) cw-EPR spectrum ($T = 150$ K). (b) Integrated cw-EPR spectrum obtained from (a). (c) Slice of ESE-detected 2D nutation spectrum at $\omega/2\pi = 5$ MHz ($T = 5$ K).

Results

The CW-EPR spectra of **3** recorded in toluene consist of three lines (1:1:1, intensity ratio) separated by $a_N = 1.52$ mT, the typical hyperfine splitting of ^{14}N of nitroxide radicals in this solvent, and six additional lines, symmetrically placed between the external lines and the central line. The six change position, intensity, and width with temperature, as shown in Figure 1. Further splitting of the external and central lines, due to the methyl and methylene protons of the nitroxide piperidine rings, is observed as well, but only in a restricted temperature range (200−260 K). They will not be considered further in this work. The frozen solution spectrum recorded at 150 K has a very complex pattern because of the anisotropies of the *g* tensor and of the hyperfine and electron dipolar interactions (Figure 2).

When derivative **3** in a toluene glassy matrix is photoexcited, a strong signal is detected. Figure 3 shows the EPR signal recorded at 120 K as a function of magnetic field and time. It is completely in absorption and can be ascribed to the superposition of two main components. The first component is responsible for part of the intense central peak which decays very slowly, and the second presents broad components sym-

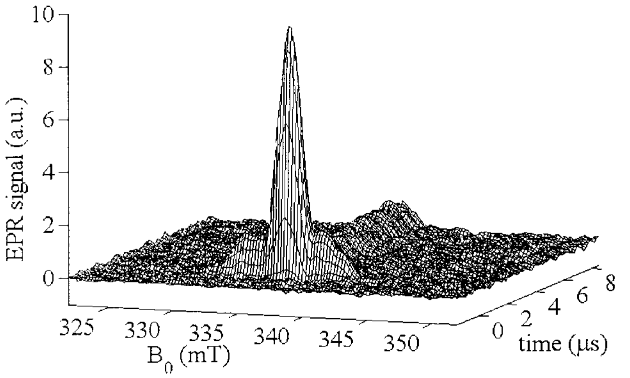


Figure 3. Field-swept time-resolved EPR spectrum of **3** in toluene solution, recorded at $T = 120$ K ($\nu_{mw} = 9.3505$ GHz).

metrically placed at high and low fields. We attribute the slow decaying component to the ground triplet state T_G and the second one to the excited quintet state Q, as confirmed by the two-dimensional EPR nutation study.

To separate and to assign the overlapping EPR signals of the species of different spin multiplicity, 2D nutation experiments were carried out according to a method already used for excited states of a similar system.[7,10] The method will be described in the following section. Figure 4A shows the 2D-spectrum recorded at 5 K, after Fourier transformation (FT) along the length of the applied microwave pulse. Mainly three nutation frequencies are observed: $\omega = 4.9$, 7.3, and 9.0 MHz. The corresponding spectra are reported in Figures 2c and 4B.

Note that the spectrum of Figure 2c is very similar to the integrated steady-state spectrum (2b) recorded at 150 K.

Discussion

Ground State. The spin Hamiltonian of a system consisting of two covalently linked nitroxide radicals, as in derivative **3**, where they are bonded to the same fullerene moiety, is

$$H = g\beta B_0(S_z^{(1)} + S_z^{(2)}) + a_N(S_z^{(1)}I_z^{(1)} + S_z^{(2)}I_z^{(2)}) - 2J_{12}S^{(1)}S^{(2)} \quad (1)$$

$S^{(1)}$ and $S^{(2)}$ are the spin operators of electrons 1 and 2 localized on the two radical groups while z indicates the component along the static magnetic field B_0. The high field approximation $g\beta B_0 \gg a_N$ is applied. The nitrogen coupling constant a_N and the g factor are considered to be the same for the two nitroxide moieties, as no difference was found in **1** and **2**.

The exchange interaction J_{12} between the two nitroxide electrons splits the electronic ground state into a singlet and a triplet. In general, for binitroxide biradicals, if $|J| \ll a_N$ a three-line spectrum is expected with a_N separation, while if $|J| \gg a_N$, the spectrum consists of five lines with intensity ratios 1:2:3:2:1 separated by $a_N/2$.[16] The measured spectra of **3** are typical of the intermediate case where J is of the same order as a_N. In this case, the magnitude of J can be evaluated from the analysis of the shape of the EPR spectrum. In fact, if J and a_N are of the same order, the EPR spectrum consists of "singlet" and "triplet" transitions. The first ones occur at field positions given by[16]

$$h\nu(\text{singlet}) = g\beta B_0 + a_N M_I/2 \pm a_N^2 \Delta m_I^2/8J \pm J \quad (2)$$

where $M_I = m_I^{(1)} + m_I^{(2)}$ is the z component of the total nuclear spin momentum and $\Delta m_I = m_I^{(1)} - m_I^{(2)}$. They are weak and not observed when the exchange interaction is modulated. In **3** a possible source of modulation is the residual rotation motion of the nitroxide *n*2 group bonded to the fulleropyrrolidine ring by a sigma bond. However, the resonance fields of the intense "triplet" transitions depend as well on J, being given by the equation[16]

$$h\nu(\text{triplet}) = g\beta B_0 + a_N M_I/2 \pm a_N^2 \Delta m_I^2/8J \quad (3)$$

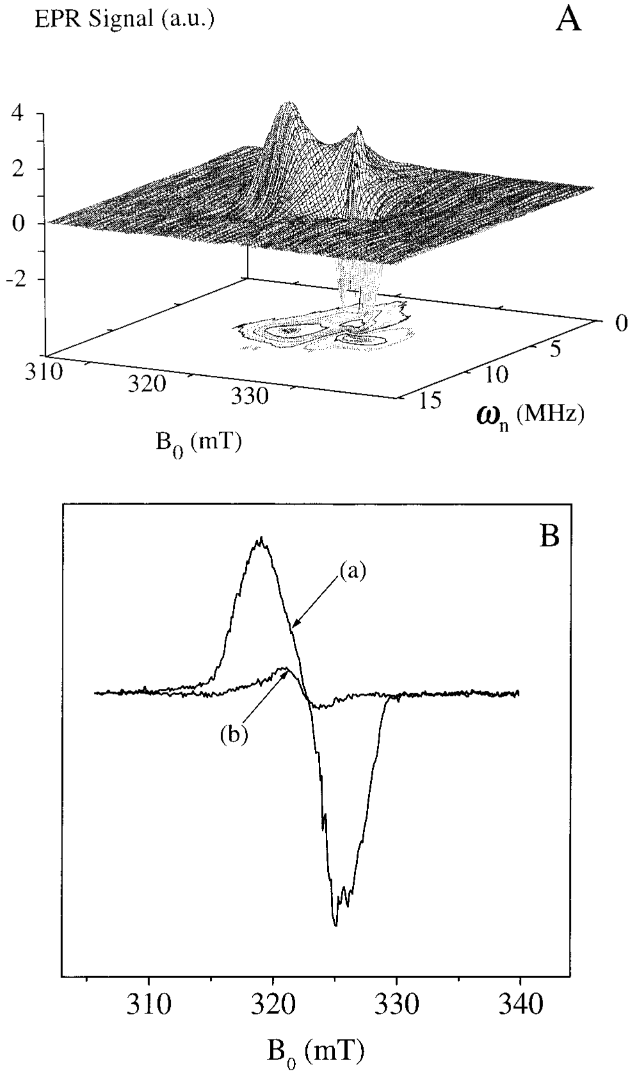


Figure 4. (A) Field-swept ESE-detected 2D nutation spectrum of **3** in toluene solution, recorded at $T = 5$ K ($\nu_{mw} = 9.0323$ GHz). (B) Slices of the surface taken at (a) 7.3 MHz, (b) 9.0 MHz.

The experimental spectra, shown in Figure 1, have been simulated using the above Hamiltonian, for various J values. The modification of the spectrum with the temperature is due to the variation of J whose values in the temperature range 360−260 K are shown in Figure 5. At $T < 260$ K it was not possible to reproduce the spectra well. Selective additional contributions to the line width due to the anisotropic terms should be considered.

Excited States. Fullerene C_{60} and its derivatives can be photoexcited by UV and visible light to excited singlet states. Intersystem crossing (ISC) from the first excited singlet to the triplet state is a very efficient process caused by spin−orbit coupling, the triplet yield being close to unity.[17]

Optical illumination of **3** produces an excited species having two unpaired electrons on fullerene which could interact with the nitroxide unpaired electrons.

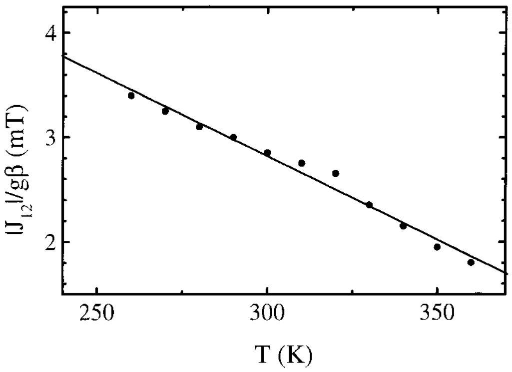


Figure 5. Temperature variation of the exchange interaction J as obtained by fitting the experimental cw-EPR spectra to eq 2.

States with total spin $S_T = 0, 1, 2$ (one singlet, two kinds of triplets and one quintet) are expected according to the different couplings between the two $S^{(1)}$,$S^{(2)} = 1/2$ nitroxide spins and the $S^{(3)} = 1$ fullerene triplet spin. Only the triplet and the quintet states can be observed in principle by EPR.

Transient nutation experiments allow for separation of the signals according to the spin multiplicity of the species.[18] They were performed, as already described,[9] by irradiating the sample with a microwave (MW) pulse of variable duration τ at fixed delay time τ_d after the laser pulse. The MW pulse rotates the sample magnetization, generated along the z axis, by an angle which depends on the MW field B_1, on the pulse duration, and on the spin multiplicity of the species. It depends also on the particular transition which is driven by the MW radiation. A subsequent spin−echo sequence allows for the measurement of M_y, the magnetization component along the y axis of the rotating frame. M_y oscillates with the nutation frequency ω_n as the first pulse duration τ is increased.

As reported in the literature, when an EPR transition between the $|S, M_s-1\rangle$ and $|S, M_s\rangle$ states is excited selectively by microwave, the nutation frequency ω_n of the transition is[19]

$$\omega_n = [S(S+1) - M_s(M_s-1)]^{1/2}\omega_1 \tag{4}$$

where ω_1 is the nutation frequency one obtains if the $-1/2$ to $1/2$ transition of a spin $S = 1/2$ species is driven with the same MW field B_1.

Since ω_n depends both on S and M_s, if the sample contains species with different spin multiplicities, they can be separated according to their nutation frequency. The individual transitions of the same species (if $S > 1$) can be separated as well. The 2D-EPR spectrum can be obtained by taking the FT along the pulse length τ of the data array consisting of the transient echo intensity measured at different magnetic fields.

In our experiments the nutation frequencies are evaluated in comparison with that of the radical Li 7,7,8,8-tetracyanoquinodimethane (Li-TCNQ, $S = 1/2$). From the FID-detected 2D nutation spectrum of Li-TCNQ, detected under the same conditions as Figure 4, we estimate $\omega_1 = g\beta B_1/\hbar$ to be 3.6 MHz. The nutation frequencies of each state are summarized in Table 1.

The spectra shown in Figures 2c and 4B are sliced ones on the 2D surface taken at 5.0, 7.3, and 9.0 MHz. These values correspond, respectively, to the nutation frequencies of the $|0\rangle \leftrightarrow |\pm1\rangle$ transitions of the triplet state T_G and of the transitions $|\pm2\rangle \leftrightarrow |\pm1\rangle$ and $|\pm1\rangle \leftrightarrow |0\rangle$ of the quintet state. The first spectrum (Figure 2c) coincides with that measured under dark conditions using the same spin−echo technique and with the integrated CW-EPR spectrum. It corresponds to the electronic ground state of the biradical species. The second and the third spectra, spin polarized in enhanced absorption at low field and in emission at high field (A/E), correspond to the quintet state transitions.

TABLE 1: Nutation Frequency ω_n for 3

$\lvert S,M_s\rangle \leftrightarrow \lvert S,M_s-1\rangle$	ω_n	$\omega_n/2\pi$ (MHz)	ω_n/ω_1[a]
$\lvert 2,\pm2\rangle \leftrightarrow \lvert 2,\pm1\rangle$ (Q)	$2\omega_1$	7.3	2.03
$\lvert 2,\pm1\rangle \leftrightarrow \lvert 2,0\rangle$ (Q′)	$\sqrt{6}\omega_1$	8.5	2.36
$\lvert 1,\pm1\rangle \leftrightarrow \lvert 1,0\rangle$ (T_G)	$\sqrt{2}\omega_1$	5	1.39

[a] $\omega_1 = 3.6$ MHz, nutation frequency of Li-TCNQ.

From the analysis of the spectra shown in Figure 4B, a value of 2.2 mT is obtained for the zero field splitting parameter $|D|/g\beta$ of the quintet state. It is worth remembering that for the outer transitions $|2,\pm2\rangle \leftrightarrow |2,\pm1\rangle$, the separation is $6|D|/g\beta$ (13.2 mT), while for the inner transitions $|2,\pm1\rangle \leftrightarrow |2,0\rangle$ it is $2|D|/g\beta$ (4.4 mT).

Spin Polarization. Spin polarization of the excited states arises from two different mechanisms: ISC due to spin−orbit coupling (SOC) and the mixing of states of different multiplicity caused by the electron dipolar interaction.[20,21] Considering photoexcited derivative **3** as a three spin system, the spin Hamiltonian describing the isotropic exchange interaction between the three paramagnetic species, excited triplet fullerene, nitroxide n1 and n2 (see Scheme 1), is

$$H_{\rm exc} = -2J_{12}S^{(1)}S^{(2)} - 2J_{13}S^{(1)}S^{(3)} - 2J_{23}S^{(2)}S^{(3)} \tag{5}$$

Let's consider first the coupling between the nitroxides (spin 1/2) to give a spin $S_{12} = 0, 1$, which is then coupled to the fullerene $S_F = 1$ spin, giving the total spin $S_T = 0, 1, 2$. Taking $S_{12} = 0$, one has a $S_T = 1$ triplet state T^a, while with $S_{12} = 1$ one has a quintet Q, a singlet S and a second triplet T^b. In the uncoupled basis they are

$$Q_{(2)} = |1,1\rangle$$
$$Q_{(1)} = (1/\sqrt{2})\,(|1,0\rangle + |0,1\rangle)$$
$$Q_{(0)} = (1/\sqrt{6})\,(2\,|0,0\rangle + |-1,1\rangle + |1,-1\rangle)$$
$$Q_{(-1)} = (1/\sqrt{2})\,(|-1,0\rangle + |0,-1\rangle)$$
$$Q_{(-2)} = |-1,-1\rangle \tag{6.1}$$

$$S = (1/\sqrt{3})\,(-|0,0\rangle + |-1,1\rangle + |1,-1\rangle) \tag{6.2}$$

$$T^b_{(1)} = (1/\sqrt{2})\,(|1,0\rangle - |0,1\rangle)$$
$$T^b_{(0)} = (1/\sqrt{2})\,(|1,-1\rangle - |-1,1\rangle)$$
$$T^b_{(-1)} = (1/\sqrt{2})\,(|-1,0\rangle - |0,-1\rangle) \tag{6.3}$$

The first value in the kets refers to the z component of the S_{12} spin, while the second one refers to the z component of the fullerene triplet spin.

To account for the spin polarization of Q observed in the EPR spectrum recorded at low temperature, we assume that z components of the nitroxide S_{12} spin are equally populated. In fact, the small Boltzmann polarization at 5 K in the magnetic field of the X-band spectrometer can be neglected. Moreover, the spin lattice relaxation is quite slow at this temperature. Therefore, the spin polarization of the Q spin sublevels is carried on only by the different populating rates of the excited fullerene triplet, contributing to the formation of Q. The selective population arises from the ISC process from the excited singlet state to the triplet state, due to spin−orbit interaction. This latter follows selection rules, which give rise in fulleropyrrolidine derivatives to zero-field triplet state populating rates in the ratios Px:Py:Pz = 1:0.24:0.03.[22] Since for these derivatives the zero-field splitting parameter D is negative, in the glassy matrix those molecules having their z axis along the magnetic field direction ($B_0 \| z$) have the triplet $|0\rangle$ population much less than those of the $|\pm 1\rangle$ states. In the high-field approximation the $|\pm 1\rangle$ populations are equal. On the contrary, if the Zeeman magnetic field is along the x or y axis, the most populated level becomes the $|0\rangle$ one.[23] The resulting triplet state EPR spectrum is in enhanced absorption for the low-field part and in emission for the high-field part.

Regarding the quintet state Q, equations 6.1 show that the contribution of the $|\pm 1\rangle$ fullerene triplet components to the quintet populations of $Q_{(\pm 2)}$, $Q_{(\pm 1)}$, and $Q_{(0)}$, are in the ratios 1:0.50:0.33, while the $|0\rangle$ component contributes in the ratios 0:0.5:0.67. Therefore, the expected polarization of the $Q_{(\pm 2)} \leftrightarrow Q_{(\pm 1)}$ and of the $Q_{(\pm 1)} \leftrightarrow Q_{(0)}$ transitions should follow the same features of the triplet spectrum, i.e., absorption/emission. Moreover, the polarization of the latter transition should be smaller than that of the former one. These expectations fit the observed spectra perfectly, as shown in Figure 4.

Concerning the polarized spectrum observed at $T = 120$ K, a new mechanism should be invoked. In fact we observe a spectrum with a net polarization in absorption at all magnetic field values. It should be noted that when the molecule undergoes rotational diffusion, the stochastic modulation of electron dipolar interaction could induce transitions between states of different spin multiplicity, analogously to the case of quartet−doublet transitions in the RTPM mechanism.[24]

The energies of the states, Q, S, T^a, and T^b at zero field are obtained from the matrix elements of the Hamiltonian (5)[25]

$$\langle Q|H_{exc}|Q\rangle = -J_{13} - J_{23} - \frac{1}{2}J_{12} \tag{7}$$

$$\langle S|H_{exc}|S\rangle = 2J_{13} + 2J_{23} - \frac{1}{2}J_{12} \tag{8}$$

$$\langle T^b|H_{exc}|T^b\rangle = J_{13} + J_{23} - \frac{1}{2}J_{12} \tag{9}$$

$$\langle T^a|H_{exc}|T^a\rangle = \frac{3}{2}J_{12} \tag{10}$$

$$\langle T^a|H_{exc}|T^b\rangle = \sqrt{2}\,(J_{13} - J_{23}) \tag{11}$$

From the TR-EPR investigation on derivatives **1** and **2** we know that $J_{13} > 0$ and $J_{23} < 0$,[8] while from Figure 5 we can estimate the magnitude of J_{12}, although its sign is unknown. At the low temperature used during the TR-EPR experiments, $|J_{12}|/g\beta \cong$ 3.5 mT.

Equations 7−11 show that if $|J_{13}| \cong |J_{23}|$, and if they have different signs, the quintet Q and the singlet S, which are eigenstates of the Hamiltonian H_{exc} (eq 5), become almost degenerate. On the other hand, the triplet states T^a and T^b are not eigenstates of H_{exc}, which strongly mixes them and gives rise to two other triplets $T^{a'}$ and $T^{b'}$. Spin polarization occurs because of spin-selective transitions of the quintet components to states having the same multiplicity as the ground states, T_G and S_G. Such transitions are caused by the stochastic modulation of the electron dipolar interaction. The rate of this process depends on the square of the matrix elements averaged over the molecular orientations and on the separation between the energies of the involved substates. The latter are determined by the Zeeman interaction and by the exchange interaction parameters J_{ij}.

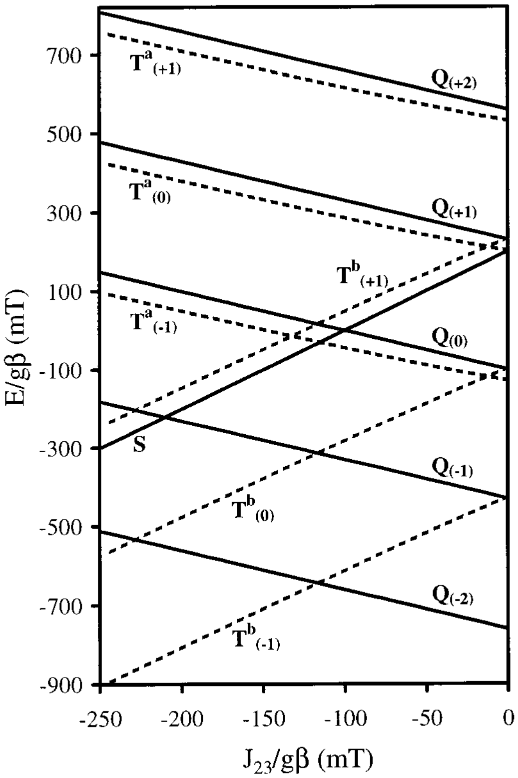


Figure 6. Energy of the Q, S, $T^{a'}$, and $T^{b'}$ excited states, calculated at $B = 330$ mT as a function of $J_{23}/g\beta$ for $J_{12}/g\beta = 3.5$ mT and $J_{13}/g\beta = 100$ mT.

Figure 6 shows the energies of the Q, S, $T^{a'}$, and $T^{b'}$ excited states, calculated at $B = 330$ mT as a function of $J_{23}/g\beta$ for $J_{12}/g\beta = 3.5$ mT and a tentative value $J_{13}/g\beta = 100$ mT. For $|J_{13}| > |J_{23}|$, quintet substates $Q_{(2)}$, $Q_{(1)}$, and $Q_{(0)}$ are closer in energy to triplet states than $Q_{(-1)}$ and $Q_{(-2)}$. Therefore, we expect a faster decay from $Q_{(2)}$, $Q_{(1)}$, and $Q_{(0)}$ than from $Q_{(-1)}$ and $Q_{(-2)}$, which give rise to an absorptive contribution to the EPR spectrum. The quintet spectrum in absorption shown in Figure 2 and the fact that we know that $J_{13} > 0$ and $J_{23} < 0$[8] agree with the hypothesis that $|J_{13}| > |J_{23}|$. This indicates that the addition of an extra bond between fullerene and nitroxide has both the effect of changing the sign and diminishing the exchange interaction.

Concerning the polarization in absorption of the ground triplet state (T_G), it could be explained by the $S \leftrightarrow T^{b'}_{(+1)}$ mixing, which feeds the ground singlet state S_G and makes $T_{G(+1)}$ become less populated than $T_{G(0)}$ and $T_{G(-1)}$.

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